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(54) **Diesel fuels.**

(57) A surfactant-free, phase-stable, aqueous fuel composition containing a diesel fuel, water, a C_1 to C_3 aliphatic alcohol or mixtures thereof and a C_4 to C_8 aliphatic alcohol or mixtures thereof, as well as the use thereof in diesel engines.

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DIESEL FUELS

Brief Summary of the Invention

Technical Field

This invention pertains to fuel compositions for use in diesel engines.

Background of the Invention

The use of diesel fuel compositions to power light-duty and heavy-duty engines and their importance throughout the world is well known. However, it is also well known that there is a definite need to decrease the exhaust emissions from such diesel-powered engines, especially in the area of visible smoke particulates and oxides of nitrogen (NO_x). In addition to satisfying obvious environmental concerns and related Environmental Protection Agency regulations, it is important to achieve a reduction in smoke/particulate formation because of its relationship to lubricating oil deterioration and attendant accelerated engine wear.

Moreover, diesel fuels are sensitive to water contamination and upon such contamination exhibit no phase stability for water even at temperatures of well above 0°C. Operational problems attendant with such water contamination are well known in the art. Thus there is also a need to improve the aqueous phase stability of diesel fuels and thereby eliminate or at least minimize the obvious operating problems that may be associated with the utilization of water contaminated diesel fuels.

Consequently, the discovery of a diesel fuel composition that would not only exhibit

decreased particulate emissions, and would also exhibit improved phase stability not only upon storage, but towards water as well, would obviously be of no small importance to the state of the art.

The search for improved diesel fuel compositions is a constant one as seen, e.g. by the following prior art.

The article "Diesel Fuel-Aqueous Ethanol Microemulsions" by A.W. Schwab et al appearing in J. Dispersion Science and Technology, 3(1), pp. 45-60 (1982) which relates to a study of two-phase mixtures of diesel fuel and aqueous ethanol as well as a detergentless system of a diesel fuel, aqueous ethanol and butanol.

U.S. Patent Application Serial No. 256,206 filed April 21, 1981 entitled "Diesel Fuel-Aqueous Alcohol Microemulsions" by A.W. Schwab available from the National Technical Information Service, PB81-248619, which is directed to hybridizing diesel fuel with high levels of water and a C_1 to C_3 alcohol which are held in a stable microemulsion at low temperatures by means of a surfactant.

The article "Microemulsions as Diesel Fuels" by G. Gillberg et al in Am. Chem. Soc. Symposium of the 172 Meeting of the American Chemical Society, San Francisco, Aug. 31 - Sept. 1, 1976 (pp 221 to 231) which discloses that emulsifiers can be used to reduce exhaust emissions in diesel fuels.

U.S. Patents 4,162,143; 4,182,614 and 4,244,701 all of which disclose methods for reducing exhaust emissions of fuel oils using aqueous emulsified fuels.

Society of Automotive Engineers (SAE) Technical Paper Series #790925 (1979), which discloses the use of water and alcoholic diesel fuel emulsions to reduce particulate exhaust emissions.

SAE Technical Paper Series #790956 (1979) which discloses a review of alcohol-diesel fuels.

SAE Technical Paper Series #810250 (1981) which discloses a study of the effect of water in diesel fuels.

SAE Technical Paper Series #810254 (1981) which discloses a study on the use of alcohol in diesel fuel emulsions.

SAE Technical Paper Series #700736 (1970) which discloses a study on the effects of emulsified fuels and water induction on diesel combustion.

It has now been discovered, for the first time, that phase-stable aqueous diesel/alcohol fuel compositions can be prepared having a cloud point of 0°C or below without the aid of surfactant emulsification and that certain of such surfactant-free, aqueous diesel/alcohol fuel compositions have also exhibited improved anti-pollutant characteristics.

Disclosure of this Invention

Thus it is an object of this invention to provide novel surfactant-free, phase-stable, aqueous diesel/alcohol fuel compositions having improved anti-pollutant characteristics. Another object of this invention is to provide a novel method (process) for preparing said diesel/alcohol fuel compositions.

More specifically, this invention is directed to a surfactant-free, phase-stable, aqueous diesel/alcohol fuel composition having a cloud point of 0°C or below, and consisting essentially of 0.1 to 1.0 weight percent water, 1 to 19 weight percent of a C_1 to C_3 aliphatic alcohol or mixtures thereof, and 1 to 18 weight percent of a C_4 to C_8 aliphatic alcohol or mixtures thereof, the remainder of said composition consisting essentially of diesel fuel.

Alternatively, this invention may be described as a method for preparing a surfactant-free, phase-stable, aqueous diesel/alcohol fuel composition suitable for use in diesel engines, which comprises mixing a diesel fuel with water, a C_1 to C_3 aliphatic alcohol or mixtures thereor and a C_4 to C_8 aliphatic alcohol or mixtures thereof, wherein said composition has a cloud point of 0°C or below, and consists essentially of 0.1 to 1.0 weight percent water, 1 to 19 weight percent of said C_1 to C_3 aliphatic alcohol or mixtures thereof, and 1 to 18 weight percent of said C_4 to C_8 aliphatic alcohol or mixtures thereof, the remainder of said composition consisting essentially of said diesel fuel.

Detailed Description

The primary component of the diesel/alcohol fuel composition of this inventions is of course a base diesel fuel which is present in a major amount. The base diesel fuel component employable in the present invention can be any conventionally known diesel fuel oil, including hydrocarbon fuel

oil mixtures having a diesel boiling range of 175°C to 400°C. Such diesel fuel oils and/or methods for their preparation are well known in the art.

The C_1 to C_3 aliphatic alcohol employable in the present invention includes methanol, ethanol, n-propanol and isopropanol, the most preferred lower alcohol being isopropanol. Of course mixtures of said C_1 to C_3 aliphatic alcohols can also be employed if desired.

The C_4 to C_8 aliphatic alcohol employable in the present invention includes butanols, pentanols, hexanols, heptanols and octanols, as well as mixtures of such alcohols, if desired. The more preferred higher alcohols are the primary alcohols of said C_4 to C_8 alcohols, especially n-butanol, isobutanol, n-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-ethylhexanol, and mixtures thereof.

It is to be understood that the surfactant-free, phase-stable, aqueous diesel/alcohol fuel compositions of this invention are single-phase, clear, transparent, homogeneous mixtures which are characterized by their thermodynamic stability over a wide range of temperatures as seen by the fact that they possess a cloud point of (at least) 0°C or below. As employed herein the term "cloud point" represents that temperature at which the fuel composition changes from a clear and transparent fluid to one which is cloudy. Moreover as noted above, the diesel/alcohol fuel compositions of this invention are "surfactant-free", i.e., no surfactant is necessary for the aqueous diesel/alcohol fuel composition of

this invention to achieve a cloud point of (at least) 0°C or below. Accordingly, the aqueous diesel/alcohol fuel compositions of this invention are not to be confused with emulsions, or even microemulsions, or diesel fuels which depend upon the presence of a surfactant to obtain their aqueous cloud point stability.

The components of the diesel/alcohol fuel compositions of this invention may be employed singularly or as mixtures and mixed in any order using any mixing or blending apparatus and technique desired. Indeed the fuel compositions of this invention are characterized by their spontaneous formation upon the proper choice and amounts of components employed. Moreover, while the selection of the various fuel composition component amounts required to achieve the results desired will be dependent upon one's experience in the utilization of the subject invention, only a minimum measure of experimentation should be necessary in order to ascertain those component amounts which will be sufficient to produce the desired results for any given situation.

For instance, in general the amount of C_1 to C_3 aliphatic alcohol or mixtures thereof present in the fuel compositions of this invention may generically range from 1 to 19 weight percent based on the total weight of the fuel composition. Likewise the generic range of the remaining components of the fuel compositions of this invention, based on the total weight of the particular fuel composition desired, include from 0.1 to 1.0 weight percent of water, the more preferred upper limit of water being about 0.7

weight percent, and from 1 to 18 weight percent of a C_4 to C_8 aliphatic alcohol or mixtures thereof, the remainder of the fuel composition consisting essentially of the base diesel fuel employed.

More specifically, preferred phase-stable fuel compositions having a cloud point of (at least) 0°C or below and containing up to 0.7 weight percent water may be obtained when the composition contains from 1 to 19 weight percent of isopropanol and about 1 to 18 weight percent of a butanol or a pentanol; and when the composition contains from 10 to 18 weight percent of isopropanol and 2 to 7 weight percent of 2-ethylhexanol.

In fuel compositions that contain a 50:50 weight percent mixture of methanol and ethanol as the lower aliphatic alcohol, preferred phase-stable compositions having a cloud point of at least 0°C or below and containing up to 0.4 weight percent water may be obtained when the composition contains from 1 to 5 weight percent of said methanol/ethanol mixture and 10 to 18 weight percent of a butanol; when the composition contains 1 to 7 weight percent of said methanol/ethanol mixture and 7 to 18 weight percent of a pentanol; and when the composition contains from 1 to 7 weight percent of said methanol/ethanol mixture and 10 to 18 weight percent of 2-ethylhexanol.

In fuel compositions that contain methanol as the lower aliphatic alcohol, preferred phase-stable fuel compositions having a cloud point of (at least) 0°C or below and containing up to

0.25 weight percent water may be obtained wherein the composition contains 1 to 5 weight percent methanol and 10 to 18 weight percent of a butanol; when the composition contains 1 to 8 weight percent of methanol and 7 to 18 weight percent of a pentanol; and when the composition contains 1 to 8 weight percent of methanol and 12 to 18 weight percent of 2-ethylhexanol.

In fuel compositions that contain ethanol as the lower aliphatic alcohol, preferred phase-stable fuel compositions having a cloud point of at least 0°C or below and containing up to 0.5 weight percent water may be obtained wherein the composition contains 1 to 7 weight percent ethanol and 10 to 18 weight percent of a butanol; when the composition contains 1 to 9 weight percent of ethanol and 8 to 18 weight percent of a pentanol; and when the composition contains 5 to 10 weight percent of ethanol and 7 to 12 weight percent of 2-ethylhexanol.

The subject invention is indeed unique and beneficial in that it provides surfactant-free, highly phase-stable, aqueous diesel/alcohol fuel compositions suitable for routine utilization in diesel engines of conventional design. Moreover, it is a common occurrence for certain unadulterated diesel fuels to appear slightly hazy on pouring, and upon standing for a few days to form a darker sediment-like layer on the bottom of the fuel which could cause operational problems such as plugging of fuel filters and injector nozzles. However, an added benefit of the diesel/alcohol fuel

compositions of this invention is their clear and transparent characteristics and the fact that they have not been found to form such sediment even upon long periods of storage.

Further, in addition to the excellent thermodynamically stable characteristics (cloud point or (at least) 0°C or below) of the diesel/alcohol fuel compositions of this invention, isopropanol containing diesel/alcohol compositions of this invention have been found to substantially reduce the amount of visible smoke and particulates as well as oxides of nitrogen (NO_x) in the exhaust emissions of the fuel compositions as compared to that of the unadulterated base diesel fuel employed. Such excellent anti-pollutant characteristics should also translate into better engine wear characteristics as well. Moreover, while the diesel/alcohol fuel compositions of this invention do possess a lower cetane number (ignition quality) than the base diesel fuel per se, such a drawback should be able to be overcome by the additional use of small amounts of any suitable conventional cetane improver such as an alkyl nitrate, if desired. Thus it is to be understood that, if desired, the fuel compositions of this invention may contain minor amounts i.e. less than 1 weight percent of any conventional cetane improver, as well as such amounts of any suitable conventional corrosion inhibitor, metal deactivator or antioxidant.

The following examples are illustrative of the present invention and are not to be regarded as limitative. It is to be understood that all of the parts, percentages and proportions referred to

herein and in the appended claims are by weight unless otherwise noted.

EXAMPLE 1

A series of fuel compositions were prepared wherein various amounts of a diesel fuel, (#2 Gulf) which had an unadulterated cloud point of -15°C, were mixed with various amounts of isopropanol, water and a 50:50 weight percent mixture of n-butanol and isobutanol and the cloud point of each composition determined as outlined below

Composition	Diesel Fuel (wt.%)	Isopropanol (wt.%)	Water (wt.%)	Mixture of n-butanol & isobutanol (wt.%)	Cloud Point °C
a)	84.13	8.74	0.59	6.54	-9
b)	81.84	8.50	0.57	9.09	-15
c)	85.66	5.43	0.72	8.20	6
d)	84.79	5.38	0.71	9.13	-5
e)	83.94	5.32	0.70	10.04	-12
f)	83.60	5.30	0.70	10.40	-15

Of the above compositions, composition "f" was most preferred because of its low cloud point and high water content. Compositions corresponding to "d", "e", and "f" were subsequently prepared using a diesel fuel [IH-CAT (Caterpillar 1G1H Reference Fuel from Howell, Hydrocarbons Inc.)] that had an unadulterated cloud point of -3°C and the aqueous cloud points of the three compositions so prepared were found to be 5°C, -2°C and -5°C, respectively. In addition a fuel composition containing about 84.78 grams (90.4 wt. %) of said #2 Gulf diesel fuel which had an unadulterated cloud point of -15°C, about 8.45 grams (9.0 wt. %) isopropanol and 0.56 grams (0.6 wt. %) water was cloudy at room temperature indicating that the contained water was not in stable form.

Example 2

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Gulf) which had an unadulterated cloud point of -15°C, with various amounts of isopropanol, water, and a mixture of primary amyl alcohols [analysis: 98.7 wt. % total primary amyl alcohol; 66.14 wt. % n-pentanol and 32.56 wt. % 2-methyl-1-butanol and 3-methyl-1-butanol]. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Isopropanol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	86.91	8.66	0.58	3.85	4
b)	84.92	8.82	0.59	5.66	-9
c)	82.59	8.59	0.56	8.26	-13
d)	85.33	8.86	0.60	5.21	-6
e)	78.75	10.75	0.66	9.84	-12
f)	84.13	8.74	0.59	6.54	-15
g)	85.73	8.90	0.60	4.76	-3

Above compositions "b", "f" and "g" were subsequently prepared using another diesel fuel [IH-CAT (Caterpillar 1G1H Reference Fuel from Howell Hydrocarbons Inc.)] having an unadulterated cloud point of -3°C. The cloud points of these three compositions so prepared were -3°C, -7°C and -1°C, respectively.

Example 3

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Gulf) which had an unadulterated cloud point of -15°C, with various amounts of isopropanol, water and iso-butanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Isopro-panol (wt.%)	Water (wt.%)	Isobutanol (wt.%)	Cloud Point °C
a)	86.91	8.66	0.58	3.85	5
b)	85.73	8.91	0.60	4.76	2
c)	84.92	8.83	0.58	5.66	-4
d)	84.13	8.74	0.59	6.54	-7
e)	82.59	8.59	0.56	8.26	-14
f)	81.84	8.50	0.57	9.09	-15
g)	81.74	7.36	0.68	10.22	-12

Three compositions corresponding to composition "e" above were prepared wherein the isobutanol was replaced with n-butanol, n-pentanol and 2-ethylhexanol, respectively, and their respective cloud points were found to be -13°C, -14°C and -7°C.

Example 4

A series of fuel compositions were prepared consisting of 81.78 wt. % of a diesel fuel, (#2 Gulf) having an unadultered cloud point of -15°C, and 8.56 wt. % of anhydrous (200 proof) ethanol, 0.57 wt. % water and 9.09 wt. % of a higher alcohol. The cloud points of said compositions were as follows.

Higher Alcohol	Cloud Point (°C)
n-butanol	14
iso-butanol	17
n-pentanol	-2
Mixture of primary amyl alcohols*	1
2-ethylhexanol	-2

*(Analysis: 98.7 wt. % total amyl alcohol; 66.14 wt. % n-pentanol and 32.56 wt. % 2-methyl-1-butanol and 3-methyl-1-butanol).

Example 5

Two fuel compositions were prepared by mixing a diesel fuel, (#2 Gulf) which had an

unadulterated cloud point of -15°C, with methanol, water and a mixture of primary amyl alcohols (analysis: 98.7 wt. % total amyl alcohols; 66.14 wt. % n-pentanol and 32.56 wt. % 2-methyl-1-butanol and 3-methyl-1-butanol). The compositions so prepared along with their cloud points were as follows:

Composition	Diesel Fuel (wt.%)	Meth-anol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	84.04	4.17	0.28	11.50	-9
b)	75.59	7.92	0.53	15.97	6

Another fuel composition consisting of 74.38 wt. % diesel fuel, (#2 Gulf) which had an unadulterated cloud point of -15°C, 7.75 wt. % methanol, 0.52 wt. % water and 17.36 wt. % isobutanol, had a cloud point of only 20°C.

Example 6

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of isopropanol, water and iso-butanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Isopro-panol (wt.%)	Water (wt.%)	Isobutanol (wt.%)	Cloud Point °C
a)	81.43	3.97	0.7	13.90	-18
b)	84.41	3.97	0.7	10.92	-14
c)	80.44	15.89	0.7	2.98	-3
d)	83.42	7.94	0.7	7.94	-8
e)	95.19	3.27	0.12	1.42	-17
f)	94.80	3.24	0.18	1.78	+3
g)	94.24	3.22	0.18	2.36	-8
h)	93.67	3.21	0.18	2.94	-16
i)	93.33	3.77	0.20	2.70	-16
j)	95.22	3.72	0.12	0.94	-9
k)	95.19	2.79	0.12	1.90	-12

l)	94.91	2.78	0.12	2.19	-17
m)	95.17	1.86	0.12	2.85	-16
n)	95.15	0.93	0.12	3.80	-16
o)	94.20	3.72	0.18	1.90	-5

Example 7

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of isopropanol, water, and a mixture of primary amyl alcohols (analysis: 98.7 wt. % total primary amyl alcohol; 66.14 wt. % n-pentanol and 32.56 wt. % 2-methyl-1-butanol and 3-methyl-1-butanol). The compositions so prepared along with their cloud points were as follows:

Composition	Diesel Fuel (wt.%)	Isopropanol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	82.00	5.30	0.70	12.00	-17
b)	82.00	14.30	0.70	3.00	-6
c)	85.50	6.80	0.70	7.00	-17
d)	86.00	11.30	0.70	2.00	+18
e)	86.00	8.30	0.70	5.00	+5
f)	94.55	4.30	0.15	1.00	+10
g)	94.07	4.29	0.15	1.49	-3
h)	93.62	4.26	0.15	1.97	-13
i)	95.19	2.79	0.12	1.90	-17

Example 8

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of isopropanol, water and 2-ethylhexanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Isopropanol (wt.%)	Water (wt.%)	2-Ethylhexanol (wt.%)	Cloud Point °C
a)	82.00	11.30	0.70	6.00	-17
b)	81.00	17.30	0.70	1.00	+2
c)	83.00	13.30	0.70	3.00	-6
d)	84.00	10.30	0.70	5.00	-4

Another fuel composition consisting of 86.25 wt. % diesel fuel, (#2 Gulf) having an unadulterated cloud point of -15°C, 8.60 wt. % isopropanol, 0.57 wt. % water and 4.58 wt. % 2-ethylhexanol had a cloud point of only 15°C.

Example 9

A series of fuel compositions were prepared wherein various amounts of diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, were mixed with various amounts of a 50:50 weight percent mixture of methanol and ethanol, water and isobutanol and the cloud point of each composition determined as outlined below

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Ethanol (wt.%)	Water (wt.%)	Isobutanol (wt.%)	Cloud Point °C
a)	80.18	2.24	2.24	0.40	14.94	-9
b)	87.64	0.80	0.80	0.40	10.36	-4
c)	87.64	1.50	1.50	0.40	8.96	+15

Example 10

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of a 50:50 wt. % mixture of methanol and ethanol, water and a mixture of primary amyl alcohols (analysis: 98.7 wt. % total amyl alcohol; 66.14 wt. % n-pentanol and 32.56 wt. % 2-methyl-1-butanol

and 3-methyl-1-butanol). The compositions so prepared along with their cloud points were as follows:

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Ethanol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	80.68	2.49	2.49	0.40	13.94	-18
b)	87.14	1.25	1.25	0.40	9.96	-18
c)	85.66	1.99	1.99	0.40	9.96	-12
d)	82.16	3.74	3.74	0.40	9.96	+8

Example 11

A series of fuel compositions were prepared wherein various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, were mixed with various amounts of a 50:50 weight percent mixture of methanol and ethanol, water and 2-ethylhexanol and the cloud point of each composition determined as outlined below

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Ethanol (wt.%)	Water (wt.%)	2-Ethyl Hexanol (wt.%)	Cloud Point °C
a)	80.27	2.79	2.79	0.40	13.75	-17
b)	82.66	3.49	3.49	0.40	9.96	+8
c)	81.68	1.99	1.99	0.40	13.94	+7
d)	81.67	2.49	2.49	0.40	12.95	-4
e)	80.87	3.39	3.39	0.40	11.95	-16

Example 12

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of methanol, water and isobutanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Water (wt.%)	Isobutanol (wt.%)	Cloud Point °C
a)	86.78	2.00	0.25	10.97	-16
b)	81.79	3.99	0.25	13.97	-10
c)	84.79	2.99	0.25	11.97	-8
d)	85.78	4.99	0.25	8.98	+27

Example 13

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of methanol, water and 2-ethylhexanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Water (wt.%)	2-Ethylhexanol (wt.%)	Cloud Point °C
a)	79.80	6.98	0.25	12.97	-16
b)	81.79	3.99	0.25	13.97	-17
c)	83.79	3.99	0.25	11.97	-8
d)	84.79	3.99	0.25	10.97	+1
e)	81.80	6.98	0.25	10.97	+6

Example 14

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of methanol, water and a mixture of primary amyl alcohols (analysis: 98.7 wt.% total primary amyl alcohol; 66.14 wt.% n-pentanol and 32.56 wt.% 2-methyl-1-butanol and 3-methyl-1-butanol). The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Methanol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	89.77	1.00	0.25	8.98	-15
b)	81.19	6.68	0.25	11.88	-18
c)	86.00	3.75	0.25	10.00	-12
d)	90.00	2.25	0.25	7.50	-10
e)	89.78	2.99	0.25	6.98	+5
f)	88.78	2.99	0.25	7.98	-10
g)	81.00	7.75	0.25	11.00	+7
h)	81.83	5.99	0.20	11.98	-12
i)	81.76	5.98	0.30	11.96	-2
j)	85.83	3.99	0.20	9.98	-13
k)	85.74	3.99	0.30	9.97	+4

Example 15

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of ethanol, water and isobutanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Ethanol (wt.%)	Water (wt.%)	Isobutanol (wt.%)	Cloud Point °C
a)	80.59	1.00	0.50	17.91	-18
b)	87.55	1.00	0.50	10.95	-10
c)	85.56	2.99	0.50	10.95	-6
d)	83.58	3.98	0.50	11.94	-11
e)	85.57	3.98	0.50	9.95	+2
f)	79.60	5.97	0.50	13.93	-13

Example 16

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of ethanol, water and a mixture of primary amyl alcohols (analysis: 98.7 wt.% total primary amyl alcohol; 66.14 wt.% n-pentanol and 32.56

wt.% 2-methyl-1-butanol and 3-methyl-1-butanol). The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Ethanol (wt.%)	Water (wt.%)	Mixture of primary amyl alcohols (wt.%)	Cloud Point °C
a)	80.59	1.00	0.50	17.91	-17
b)	86.56	1.99	0.50	10.95	-17
c)	79.59	8.96	0.50	10.95	-16
d)	81.58	8.96	0.50	8.96	-5
e)	85.56	4.98	0.50	8.96	-12
f)	85.57	5.97	0.50	7.96	+2

Example 17

A series of fuel compositions were prepared by mixing various amounts of a diesel fuel, (#2 Phillips Petroleum) which had an unadulterated cloud point of -18°C, with various amounts of ethanol, water and 2-ethylhexanol. The compositions so prepared along with their cloud points were as follows.

Composition	Diesel Fuel (wt.%)	Ethanol (wt.%)	Water (wt.%)	2-Ethyl-hexanol (wt.%)	Cloud Point °C
a)	82.58	6.97	0.50	9.95	-17
b)	83.57	6.97	0.50	8.96	-4
c)	81.59	9.95	0.50	7.96	-2
d)	83.57	8.96	0.50	6.97	+8

Example 18

A fuel composition designated "D_4," which consisted of 83.60 wt.% of a diesel fuel [IH-CAT (Caterpillar 1G1H Reference Fuel from Howell Hydrocarbon Inc.)] which had an unadulterated cloud point of -3°C, 5.30 wt.% of isopropanol, 0.70 wt.% water and 10.40 wt.% of 50:50 wt.% mixture of n-butanol and isobutanol, said

composition "D_4" having a cloud point of -5°C., along with another composition designated "D_5" which consisted of 85.73 wt.% of the same diesel fuel employed in composition D_4, 8.90 wt.% of isopropanol, 0.60 wt.% water and 4.76 wt.% of a mixture of primary amyl alcohols (analysis: 98.7 wt.% total amyl alcohol; 66.14 wt.% n-pentanol and 32.56 wt.% 2-methyl-1-butanol and 3-methyl-1-butanol), said composition "D_5" having a cloud point of -1°C., were prepared and evaluated versus the same unadulterated base diesel fuel employed in preparing each composition D_4 and D_5 in terms of exhaust emissions and fuel economy.

The performance tests were conducted on a 6 cylinder diesel engine geared to a dynamometer capable of loading the engine to 500HP wet gap. The performance of fuel composition D_4 was compared with the performance of the base diesel fuel at two engine modes : (a) 1200 RPM/(557 lbs.) 251 kg load (which corresponds to an engine operation in a very rich fuel (excess fuel) Mode) and (b) 1400 RPM/(600 lbs.) 270 kg load (which corresponds to a normal operation of the engine under considerable load (e.g. climbing a hill). The performance of fuel composition D_5 was also compared with the performance of the base diesel fuel at engine modes (a) 1200 RPM/(560 lbs.) 252 kg load and (b) 1400 RPM/(605 lbs.) 272 kg load. In addition the performance of composition D_5 was assessed at an engine mode (c) 2090 RPM/(475 lbs.) 214kg load as compared to the base diesel fuel at an engine mode of 2084 RPM/(508 lbs.) 229 kg load (which corresponds to an engine operation at high speed and high load).

The test results are reported below : all fuel economy values being an average of five measurements; all smoke measurements being an average of five measurements and all particulate measurements being an average of three measurements.

Fuel Consumption (lbs./hour) kg/h

Operating Mode RPM/(lbs) kg		Base Diesel Fuel	Fuel Comp. D-4	Fuel Comp. D-5
1200/(557)	251	(83.20)37,44	(87.02)39,16	-
1200/(560)	252	(83.10)37,39	-	(84.91)38,21
1400/(600)	270	(101.98)45,89	(105.14)47,31	-
1400/(605)	272	(100.36)45,16	-	(101.99)45,90
2084/(508)	229	(132.51)59,63	-	-
2090/(475)	214	-	-	(127.5) 57,37

Particulates (Grams)

Operating Mode RPM/(lbs)kg		Base Diesel Fuel	Fuel Comp. D-4	Fuel Comp. D-5
1200/(557)	251	0.0163	0.0174	-
1200/(560)	252	0.0175	-	0 .0167
1400/(600)	270	0.0104	0.0061	-
1400/(605)	272	0.0140	-	0 .0143
2084/(508)	229	0.0024	-	-
2090/(475)	214	-	-	0 .0014

Smoke (% Opacity)

Operating Mode RPM/(lbs) kg		Base Diesel Fuel	Fuel Comp. D-4	Fuel Comp. D-5
1200/557	251	12.74	11.9	-
1200/560	252	12.74	-	11.8
1400/600	270	9.30	5.06	-
1400/605	272	9.38	-	7.52
2084/508	229	2.18	-	-
2090/475	214	-	-	1.64

The above data shows that operation of the engine with fuel compositions D_4 and D_5 of this

invention resulted in a significant reduction in both smoke opacity and particulate content of the exhaust over that shown when employing the base diesel fuel if the engine is not strained to a maximum. As seen the average decrease in smoke opacity for D_4 at modes 1200/($\overset{251}{557}$) and 1400/($\overset{270}{600}$) was 6.3% and 45% and for D_5 at modes 1200/($\overset{252}{560}$) and 1400/($\overset{272}{605}$) was 7.1% and 20.2%. Likewise the average decrease in particulate content for D_4 at mode 1400/($\overset{270}{600}$) was 41.3% (mode 1200/($\overset{251}{557}$) showing an average increase of 6.7%) and for D_5 at mode 1200/($\overset{252}{560}$) was 4.6% (mode 1400/($\overset{272}{605}$) showing an average increase of 2.1%). It should be noted that smoke and particulate formation is a complex phenomena, so these measurements will not necessarily always coincide. However, it is possible to have both reduced opacity in smoke emission, and at the same time, a decrease in particulate emission. Moreover due to the inherent difficulties with particulate analysis one should consider trends in the data and not absolute values. While operation with D_4 at modes 1200/($\overset{251}{557}$) and 1400/($\overset{270}{600}$) showed an average loss in fuel economy of 4.6% and 3.0% respectively, and operation of D_5 at modes 1200/($\overset{252}{560}$) and 1400/($\overset{272}{605}$) showed an average loss in fuel economy of 2.2% and 1.6% respectively. However, with D_4 the variation in fuel consumption is good compared to what industry accepts as a variation. Moreover the engine ran quite well with the D_4 and D_5 fuels.

Moreover, while a one to one comparison between the data of D_5 at mode 2090/($\overset{214}{475}$) and the base diesel fuel at mode [illegible]84/($\overset{229}{508}$) cannot be made since the data can not be normalized because the fuel consumption of D_5 was less than the base fuel

and D_5 was not pulling the same engine load as the base fuel and thus had a different power performance, which makes it difficult to say just how large the effect is, nonetheless it is clear that D_5 exhibited a significant positive effect on smoke and particulate emission and also on the fuel consumption as seen by its unnormalized average increase of 3.8% in fuel economy and unnormalized average decreases of 27.3% in smoke opacity and 42% in particulate content of the exhaust.

Example 19

The physical properties as listed in ASTM-D975, except for cetane number, water and sediment, of fuel compositions D_4 and D_5 as well as of the base diesel fuel (IH-CAT) employed in Example 18 are listed below.

Physical Properties

	D-4	D-5	IH-CAT
Flash Point, °C	7	13	77
Cloud Point, °C	-8	-8	-7
Carbon Residue, %	0.21	0.21	0.06
Ash, wt. %	0.01	<0.005	0.003
Viscosity at 40°C, mm²/s	2.97374	2.95754	3.31@100°C
Sulfur, wt. %	0.3717	0.3608	0.399
Copper Strip Corrosion	1-A	1-A	1-A
Distillation, °C			
Initial Boiling Point, °C	79	80	200
10% Evaporated	102	93	240
20% Evaporated	182	182	253
50% Evaporated	260	260	269
90% Evaporated	305	305	321
End Point, °C	335	321	350
% Recovered	98	97.5	99.0
% Residue	1.5	1.5	1.0
% Loss	0.5	1.0	0

The above evaluation shows that fuel compositions D_4 and D_5 of this invention meet all the standard specifications for No. 2 diesel

fuels (ASTM-D-975) except for the flash point. Another evaluation of the flash points of D-4, D-5 and the IH-CAT showed 26,5 , 20 and 76°C respectively.

Example 20

A fuel composition designated "D_6" consisting of about 83.60 wt. % of a diesel fuel, (#2 Phillips Petroleum) which had a cloud point of -18°C, 5.30 wt. % of isopropanol, 0.70 wt. % water and 10.40 wt. % of a 50:50 wt. % mixture of n-butanol and isobutanol said composition having a cloud point of -18°C, along with a fuel composition designated "D_7" which was the same as composition "D_6", but also contained 0.15 wt.% of a commercial cetane improver (an alkyl nitrate) were prepared and evaluated versus the same unadulterated base diesel fuel employed in preparing each composition D_6 and D_7 in terms of exhaust emissions and fuel economy. The performance tests were conducted on a chassis-mounted 5.7 liter Oldsmobile and followed standard cold-start Federal Test Procedures (CFR, Title 40, Part 86, SubPart B). The results of said tests based on an average of duplicate runs for each fuel were as follows:

Fuel	Cetane Number	EMISSIONS (g/mile) km: Particulates	NO_x	Hydro-carbons	Carbon Monoxide	MPG
Base Diesel	48	(0.389) 0,243	(1.34) 0,837	(0.327) 0,204	(1.21) 0,756	(21.3) 13,3
D_6	40	(0.311) 0,194	(1.27) 0,794	(0.390) 0,244	(1.46) 0,912	(21.2) 13,2
D_7	46	(0.322) 0,201	(1.27) 0,794	(0.386) 0,241	(1.40) 0,875	(21.4) 13,4

The above results show that operation of the engine with fuel compositions D_6 and D_7 of this invention resulted in a significant reduction in both particulates and oxides of nitrogen in the

exhaust over that shown when employing the base diesel fuel; while fuel economy remained essentially the same.

Claims

1. A surfactant-free, phase-stable, aqueous diesel/alcohol fuel composition having a cloud point of $0^{o}C$ or below and consisting essentially of

a) a diesel fuel,

b) 0.1 to 1.0 weight percent water,

c) 1 to 19 weight percent of a C_1 to C_3 aliphatic alcohol or mixtures thereof, and

d) 1 to 18 weight percent of a C_4 to C_8 alcohol or mixtures thereof.

2. A composition as defined in claim 1, wherein the component c) is isopropanol and wherein the composition contains up to about 0.7 weight percent water.

3. A composition as defined in claim 2, wherein the component d) is selected from the group consisting of n-butanol, isobutanol, 2-methyl-1-butanol, 3-methyl-1-butanol, n-pentanol and 2-ethylhexanol, or mixtures thereof.

4. A composition as defined in claim 3, wherein the component d) is isobutanol or n-butanol or a mixture of n-butanol and isobutanol or a mixture of primary amyl alcohols or 2-ethylhexanol, or n-pentanol.

5. A composition as defined in claim 1 to 4 wherein the component c) is methanol or ethanol or a mixture of methanol and ethanol.

6. A composition as defined in claim 1 to 5 wherein an alkyl nitrate cetane improver is also present in said composition.

7. The use of the surfactant-free, phase-stable, aqueous diesel/alcohol fuel composition as claimed in claim 1 - 6 for use in diesel engines.